

**Benzo[*a*]pyrene, Phenols and other
Products from Pyrolysis of the
Cigarette Additive, (*d,l*)-Menthol**

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THIS communication surveys the chief products from the thermal degradation of (*d,l*)-menthol and discusses some qualitative and quantitative differences in product composition at two selected temperatures. The thermal decomposition of menthol—a naturally occurring alcohol—is of special significance because of its extensive use as a commercial additive, particularly in tobacco products.

Preliminary studies were undertaken to determine whether menthol, because of its structural characteristics, could serve as a phenol-precursor. Phenols are considered to be significant contributors to the flavour and aroma of tobacco smoke¹, and have been reported to enhance the carcinogenic activity of certain polynuclear aromatic hydrocarbons². By examining the pyrolytic products of menthol, we sought to establish what contribution, if any, this additive might make towards the chemical, and consequently the biological, properties of tobacco smoke. Its effect on the flavour of such smoke is, of course, well known.

Commercially obtained samples of gas chromatographically purified (*d,l*)-menthol (K and K Laboratories, Inc.) were pyrolysed in horizontal quartz tubes (4 ft. x 1.25 in., *O.D.*) packed with quartz chips under a stream of dry nitrogen (30 ml./min). The first experiments were performed at $860 \pm 5^\circ \text{C}$, the reported burning temperature of a cigarette³. For proper perspective, however, and in order to examine the effect of temperature on pyrolysate composition, this procedure was repeated at $600 \pm 5^\circ \text{C}$.

Pyrolysates were condensed in a series of cooled (dry ice/acetone) glass traps, and recovered by repeated extractions with diethyl ether and 0.5 per cent aqueous sodium hydroxide. Phenols were thus recovered as the sodium salts, and subsequently converted to free phenols by adjusting the pH of the basic extract to 6.8 with a stream of carbon dioxide. Ultimately, the phenols were obtained in small volumes of dry ether suitable for gas chromatographic analysis. Table 1 summarizes the quantitative data for the three chief phenols obtained in the experimental conditions used. That more than six times the amount of phenol was produced at the simulated burn temperature of a cigarette suggested a more extensive examination of the total product composition of the pyrolysates obtained at the two temperatures. Accordingly, the data obtained from a gas chromatographic survey of the components of the neutral fraction are presented in Table 2.

Table 1. PHENOLS FROM PYROLYSIS OF MENTHOL*

	600° C	860° C
Phenol	29	192
<i>o</i> -Cresol	5	3
<i>m</i> - and/or <i>p</i> -Cresol†	13	14

* Values in mg/100 g menthol pyrolysed. Identifications based on co-injection data; phenol confirmed by spectral analysis (infrared, ultraviolet).

† Not separable under the GLC conditions used.

Table 2. PERCENTAGE PRODUCT* IN PYROLYSATE FROM MENTHOL

Product†	600° C	860° C
Benzene	11.9	17.5
Toluene	16.3	13.2
Ethylbenzene	1.9	7.7
Styrene	—	12.0
3-Methylcyclohexanone	20.1	2.4
"Vinyl methylcyclohexanone"	33.8	5.7
<i>p</i> -Cymene	—	6.2
Naphthalene	—	9.6
"Alkyl naphthalenes"	—	3.7
Biphenyl	—	2.8
Acenaphthylene	—	2.2
Anthracene/phenanthrene	—	3.8
Unidentified products	15.9	13.2

* Gas chromatographable neutrals; recovered menthol not included (see text).

† In order of retention time on 5 ft. × 0.25 in. O.D. columns of 20 per cent SE-30 on 'Chromosorb W'; column temperature programmed from 70° to 250° C at 6° C/min*. Identifications based on spectral data (mass, infrared and/or ultraviolet), and co-injection studies.

At 600° C, unreacted menthol makes up a substantial portion (78 per cent) of the neutral fraction. Characterization of the major product formed (approximately 33 per cent of the menthol-free gas chromatographable neutrals) was attempted as follows. The product formed a red-orange 2,4-dinitrophenyl hydrazone (melting point 129° to 132° C). The infrared spectrum showed strong absorption at 1,705 cm⁻¹ (indicative of carbonyl function) and weaker absorption at 895 cm⁻¹ (indicative of vinyl unsaturation). Mass spectral analysis gave a parent peak at 138. Assuming a substituted cyclohexanone with an empirical formula C₈H₁₄O, evidence would strongly indicate this product to be a vinyl methylcyclohexanone. Loss of a molecule of methane from the propyl side chain of menthol would account for the vinyl unsaturation. The positively identified 3-methylcyclohexanone and aromatic hydrocarbons are apparently products resulting from more extensive degradation of the starting material.

Pyrolyses conducted at 860° C resulted in a more highly complex product composition, unreacted menthol accounting for only 16 per cent of the neutral fraction. The appearance of certain polycyclic hydrocarbons is indicative of free radical mechanisms not in evidence at the lower experimental temperature; for example, phenyl radicals giving rise to biphenyl, and styryl radicals leading to naphthalene, and ultimately to more highly condensed ring systems⁴.

Identification of polyaromatic hydrocarbons not amenable to gas chromatographic analyses was accomplished by paper chromatographic techniques⁵. Aliquots of the

pyrolysate of menthol (860° C) were streaked on acetylated filter paper (S and S) and developed in an ascending system of ethanol : toluene : water (17 : 4 : 4). The presence of pyrene, benzo[*a*]-pyrene, and benz[*a*]anthracene was indicated by R_F values and subsequently confirmed by ultraviolet absorption spectroscopy of the eluted zones. The presence of fluoranthene was strongly indicated by R_F value and fluorescence in ultraviolet light, but could not be confirmed by spectral analysis.

In the light of previous reports concerning the tumorigenic properties of benzo[*a*]pyrene, we felt that a quantitative estimation of this component in menthol pyrolysate would prove interesting. Accordingly, we used a thin-layer chromatographic procedure⁶ using plates of 'Silica G', and *n*-hexane/diethyl ether (19 : 1) as the developing medium. The amount of benzo[*a*]pyrene produced was estimated by measuring absorbance at 363 mμ. Concentrations were obtained from a calibration curve prepared from a series of known benzo[*a*]pyrene solutions subjected to thin-layer chromatography in identical conditions. Approximately 400 μg of benzo[*a*]pyrene was obtained/g of menthol pyrolysed at 860° C. No evidence was obtained for the presence of benzo[*a*]pyrene or other polyaromatic hydrocarbons in pyrolysates produced at the lower temperature.

The contribution of menthol to the chemical and biological effects of cigarette smoke, however, must be weighed in relation to the amount used as an additive, and the amount that undergoes pyrolytic conversion. In this study, nine times as much menthol was recovered at the lower temperature (600° C) of pyrolysis than at the higher one (860° C). A previous report has indicated that only about 20 per cent of the menthol used as a cigarette additive is recovered in the mainstream smoke⁹.

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